

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Stable Despersible Accelerator Masterbatch for Use in the Vulcanization of Natural or Synthetic Rubber

We, THE GENERAL TIRE & RUBBER COMPANY, a Corporation organized under the Laws of the State of Ohio, United States of America, of 1708 Englewood Avenue, Akron, County of Summit, State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly 10 described in and by the following statement:—

The present invention relates to a method of preparing an easily dispersible vulcanizing type of accelerator for use in the vulcanization of natural or synthetic rubber. It relates specifically to substituted thiuram polysulfide compositions.

The desirability of incorporating accelerators of vulcanization into rubber compounds 20 by first preparing a masterbatch of such accelerators (i.e., a rubber mixture containing dispersed therein a higher than normal concentration of accelerator) and then masticating the masterbatch into the desired rubber compound has long been recognized. The use of the masterbatch technique is considered to provide a better degree of dispersion than is readily obtained by the addition of accelerator directly to the final rubber 30 composition. It also prevents a high concentration of accelerator and curing agent from occurring at a given place.

Masterbatches of various accelerators have been made both by the process of latex compounding wherein the accelerator is added to the latex and the coagulum dried and then masticated or masticated and dried, and by the mass compounding process wherein the accelerator is merely mixed by mastication 40 into solid rubber. While masterbatches of most accelerators prepared by either method are suitable for most purposes masterbatches of the class of rubber accelerators known as the substituted thiuram polysulfides when 45 prepared have caused considerable diffi-

[Price 3/-]

culties. This class of accelerator is both an accelerator and vulcanizing agent. It carries its own sulfur so that when the concentration of accelerator is sufficiently large to provide the acceleration required when the 50 masterbatch or accelerator is to be later added to rubber batches to prepare usable rubber compounds, curing of the rubber in the masterbatch has invariably taken place even at room temperature on standing with 55 the result that the masterbatch itself could not be suitably dispersed in the rubber forming the base for the final usable compound. The alternative was to use the masterbatch quickly. 60

In accordance with the present invention, a process of making a masterbatch of a curing type of accelerator, comprises mixing a latex of a vulcanizable polymer or copolymer of an conjugated diolefinic compound of less 65 than 8 aliphatic carbon atoms with an aqueous slurry of a solid water-insoluble substituted thiuram polysulfide accelerator, coagulating the mixture thus formed, drying the coagulum while maintaining a tempera- 70 ture below the melting point of said substituted thiuram polysulfide and maintaining said coagulum in an unmasticated condition.

It is thought that solid water-insoluble substituted thiuram polysulfides, when incor- 75 porated in accordance with the process of the invention, apparently do not get into vulcanizing contact with rubber particles of the latex coagulum unless the coagulum is either subjected to temperatures above the 80 melting point of the solid substituted thiuram polysulfide accelerator or is subjected to mastication to cause smearing of the accelerator particles into vulcanizing contact with the rubber. Accelerator masterbatches of 85 tetra-methyl-thiuram disulfide, for example, prepared by the above outlined prior methods either by incorporation first with the latex or first in solid rubber by the mastication route, were completely set up and un- 90

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usable after a month's storage at room temperature; whereas masterbatches prepared in the examples given hereinafter, where neither mastication nor drying at sufficiently elevated temperatures to cause melting of the accelerator was used in their preparation, had, when stored for 18 months, no perceptible set up and were in excellent condition.

Thus, further in accordance with the present invention, a vulcanization accelerator masterbatch for addition to a natural or synthetic rubber during the compounding of the same, comprises an unmasticated, unvulcanized polymer or copolymer of a conjugated diolefinic compound of less than 8 aliphatic carbon atoms and at least one water insoluble solid substituted thiuram polysulfide accelerator, said masterbatch being further characterized by being usable as a vulcanization accelerator after a period of storage of at least one month at normal temperatures.

The accelerators suitable for use in the present invention are any of the substituted thiuram polysulfides, including the tetra-methyl thiuram disulfide which melts at a temperature of about 146°C. to 148°C., the dipentamethylene thiuram tetrasulfide having a melting point of 112°C., and tetra-methyl thiuram tetrasulfide and any other solid water insoluble substituted thiuram polysulfides.

In the operation of the masterbatches of the present invention the accelerator is made of an aqueous slurry by either wetting the dry powder with sufficient water to completely wet the particles thereof or preferably making a slurry of the previously undried filter cake obtained from the preparation of the accelerator. When the undried filter cake is utilized, an exceedingly small particle size and superior dispersion may be obtained without necessity for a grinding or ball milling operation. Such a dispersion is more desirable than one obtained by using a slurry formed by simply wetting and pulverizing a previously dried accelerator although the latter may be used to prepare the slurry. The amount of water required in the slurry is not critical except that it is desirable that the particles be completely wetted so that they will be miscible with the latex without causing incipient coagulation, and a thin paste-like slurry is usually preferred. Examples of the latex utilized as a binding agent for the masterbatch are butadiene, isoprene, chloroprene, and the copolymers of one or more diolefinic compounds of less than 8 aliphatic carbon atoms with one or more copolymerizable mono-olefines such as the hydrocarbon olefines, styrene and alpha methyl styrene, vinyl toluene, substituted olefines such as chlorinated styrenes, acrylo and methacrylonitriles, methyl methacrylate and other esters and

amides of acrylic and methacrylic acids, methyl-vinyl and methyl-isopropenyl ketones, vinyl pyridine and the like.

The proportion of rubber latex to accelerator in the masterbatch may vary widely as desired, the higher the percentage of rubber therein the easier the dispersion of the accelerator in the rubber mix without danger of local curing during the masticating process. It is generally uneconomical to use less than 25% of accelerator in the masterbatch composition and the benefits of dispersion and low concentration of masterbatches are decreased too greatly for most applications when the amount of the accelerator in the masterbatches is much greater than 75% of the weight of the masterbatch. In making the masterbatch the proportions of the latex and of the slurry are preferably selected so that the solids and the latexes will be in the above percentage limits. All of the solids are considered to appear in the coagulum upon coagulation of the latex mixture.

The slurry of the accelerator and of the latex are thoroughly mixed and the mixture thereafter coagulated by any desirable method as, for example, by simply making the latex mixture unstable as by the addition thereto of electrolyte such as an acid and/or salt, for example aluminium sulfate, sodium chloride or acetic acid. By "acid" is meant a material which has a pH value of less than 7 in aqueous solution. Coagulation may also be accomplished without the use of these coagulating agents by simply drying the latex-vulcanizing agent mixture in a thin form section under a reduced pressure to remove water. By utilizing a relatively large amount of the accelerator having a small particle size, the surface area of the accelerator is sufficiently large to provide a coagulum in the form of a crumb which dries relatively easily and is exceptionally desirable from the standpoint of ease of dispersion when the masterbatch is added as a compounding agent in the preparation of rubber mixes. During drying it is exceptionally important that the temperature be maintained below the melting point and preferably below the softening point in the accelerator. In the case of the lower melting accelerators, the commercial drying operations are generally accomplished at reduced pressure and at a temperature which is only slightly elevated. Mastication of the coagulum, after drying has progressed to a considerable degree, is undesirable and is likely to cause vulcanizing contact of the rubber with the accelerator.

The following examples, in which parts are by weight, illustrate the present invention.

EXAMPLE 1

parts
Wet filter cake of tetramethyl-thiuram disulfide (containing about 67%)

130

solids and about 33% water).
Butadiene-styrene copolymer latex
(containing about 33% solids which
contain about 28% combined sty-
rene).
Water 600
The wet filter cake is mixed into the water
to form a slurry and a slurry is then added
with stirring to the above latex. After the
10 latex and the slurry are thoroughly mixed,
200 parts of a 10% solution of sodium
chloride is added to the above mixture with
stirring and a 3% solution of sulfuric acid is
stirred into the mixture a little at a time until
15 coagulation is complete. The coagulum is
then separated from the liquid by filtering
and the coagulum washed by spraying it with
water while it is on the filter. The filtered
20 product thus obtained is placed upon trays
in a vacuum oven and heated to 80°C. under
reduced pressure, preferably about 100 mm
of mercury or less, until drying of the co-
agulum is substantially complete. The co-
agulum thus obtained is packed in bags for
25 sale as a masterbatch.

A sample taken from the masterbatch
above prepared was placed in a polyethylene
bag and stored for one and one-half years at
room temperature. When, after this elapsed
30 time, it was examined it showed no signs of
any deterioration whatsoever. It dispersed
very readily in rubber and had high acceler-
ation activity.

EXAMPLE 2

35 The wet filter cake in the above Example
1 was substituted by 200 parts of pulverized
tetramethyl thiuram disulfide. This material
was then stirred into 500 parts of water con-
taining 0.5% of wetting agent, such as an
40 alkyl aryl sulfonate, dissolved therein. The
slurry was then mixed with GR-S type 2
latex in the same manner as was the slurry
of Example 1. Other conditions remained
substantially the same. The coagulum ob-
45 tained after drying at a temperature well
below 100°C. is easily dispersible in rubber
and has exceptional storage ability. The
particle size of the masterbatch was some-
what larger in the case of Example 1 than in
50 the case of Example 2. All or part of the
tetramethyl thiuram disulfide in the above
Example or any of the other water insoluble
solid substituted thiuram disulfide acceler-
ators may be substituted to provide master-
55 batches suitable for compounding into rubber
mixes.

The tetramethyl thiuram disulfide is the
preferred accelerating material, however.
The latex used in the above Example may
60 be substituted by latices of other rubbery
polymers of conjugated diolefinic compounds
of less than 8 aliphatic carbon atoms, either
natural or synthetic as above mentioned,
rubber polymers being here considered as
65 those which are vulcanizable (of course after
a curing type of accelerator, substantially as 130

300 suitable compounding) to a soft rubbery
state.

In the above two Examples there is pro-
duced a masterbatch of solid substituted
thiuram polysulfide accelerator which may 70
be stored for long periods of time without
causing incipient vulcanization of the rubber
thereof; even though the percentage of accel-
erator to rubber in the masterbatch is large.

Furthermore, the said two Examples, show 75
a method of making easily dispersible solid
substituted thiuram polysulfide accelerator-
rubbery polymer compositions suitable for
incorporation into rubber compounds to
provide vulcanization acceleration thereof 80
which easily dispersible compositions do not
deteriorate upon relatively long storage such
as one year or even more.

It is to be understood that variations and
modifications of the specific invention here- 85
in shown and described may be made with-
out going outside the scope of the invention.

What we claim is:—

1. A process of making a masterbatch of
a curing type of accelerator, which com- 90
prises mixing a latex of a vulcanizable poly-
mer or copolymer of a conjugated diolefinic
compound of less than 8 aliphatic carbon
atoms with an aqueous slurry of a solid
water insoluble substituted thiuram poly- 95
sulfide accelerator, coagulating the mixture
thus formed, drying the coagulum while
maintaining a temperature below the melting
point of said substituted thiuram poly-
sulfide and maintaining said coagulum in an 100
unmasticated condition.

2. A process according to Claim 1, wherein
said substituted thiuram polysulfide is
tetramethyl thiuram disulfide.

3. A process according to either of Claims 105
1 and 2, wherein the copolymer is a copoly-
mer of butadiene and styrene.

4. A vulcanization accelerator master-
batch for addition to a natural or synthetic
rubber during the compounding of the same, 110
comprising an unmasticated, unvulcanized
polymer or copolymer of a conjugated diole-
finic compound of less than 8 aliphatic
carbon atoms and at least one water in-
soluble solid substituted thiuram polysulfide 115
accelerator, said masterbatch being further
characterized by being, usable as a vulcani-
zation accelerator after a period of storage of
at least one month at normal temperatures.

5. An accelerator masterbatch according 120
to Claim 4, comprising 25 to 75 parts by
weight of the polymer or copolymer and 75
parts by weight of the accelerator.

6. A masterbatch according to either of 125
Claims 4 or 5 in crumb-like form.

7. A masterbatch according to any of
Claims 4, 5 and 6, wherein said acceler-
ator is tetramethyl thiuram disulfide.

8. A process of making a masterbatch of 130
a curing type of accelerator substantially as

described herein with particular reference to any one of the Examples.

9. An accelerator masterbatch for addition to a rubber during the compounding of same substantially as described herein with par-

ticular reference to any one of the Examples.

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